(5) D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Am. Chem. Soc.*, **85**, 1944 (1963); C. G. Overberger, M. Valentine, and J.-P. Anselme, *ibid.*, **91**, 687 (1969).

(6) (a) L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *J. Am. Chem. Soc.*, **93**, 1984 (1971); (b) C. P. Casey and R. A. Boggs, *ibid.*, **94**, 6457 (1972); (c) H. M. Frey and D. H. Lister, *J. Chem. Soc. A*, 627 (1970).

(7) W. L. Mock, I. Mehrotra, and J. A. Anderko, *J. Org. Chem.*, **40**, 1842 (1975).

(8) L. M. Stephenson and J. I. Brauman, *J. Am. Chem. Soc.*, **93**, 1988 (1971).

(9) R. G. Bergman in "Free Radicals", J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 5.

(10) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

(11) (a) S. G. Cohen, R. Zand and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961); (b) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); (c) J. A. Berson, E. Petrillo, Jr., and P. Bickart, *ibid.*, **96**, 636 (1974); J. A. Berson, S. S. Olin, E. W. Petrillo, Jr., and P. Bickart, *Tetrahedron*, **30**, 1639 (1974).

(12) Diels–Alder addition[13] of *trans,trans-* and *cis,trans*-hexa-2,4-diene to dimethyl azodicarboxylate, followed by hydrogenation, afforded the *cis-* and *trans*-diurethane precursors[14] (99 and 97% isomerically pure[16]).

(13) J. A. Berson and S. S. Olin, *J. Am. Chem. Soc.*, **91**, 777 (1969).

(14) Hydrolysis of the diurethanes followed by decarboxylation was carried out under an inert atmosphere (N_2) using thoroughly degassed solvents and the *cis-* and *trans*-hydrazine products were distilled on a vacuum line (10^{-4} Torr). Oxidation of the pure hydrazines in benzene-d_6 to the corresponding azo compounds was accomplished by treatment with oxygen and monitored by NMR.[15] For pyrolysis, these solutions were injected into an evacuated Pyrex chamber (preheated to 306 and 439°) and the products were collected in a trap at −196°. The product ratios were determined by electronically integrated analytical vapor phase chromatography (VPC) analysis.

(15) We thank Dr. E. Petrillo, Jr.,[11c] for helpful suggestions during the course of this work.

(16) Treatment of the diurethanes with $LiAlH_4$ afforded the corresponding tetramethylhexahydropyridazines[17] which were analyzed by analytical vapor phase chromatography.

(17) S. F. Nelson and P. J. Hintz, *J. Am. Chem. Soc.*, **94**, 7108 (1972); J. E. Anderson and J. M. Lehn, *ibid.*, **89**, 81 (1967).

(18) Surface effects were checked. None was found. Control experiments show that the hydrocarbon products are stable under the pyrolysis conditions. Hydrazone by-product was shown not to give cyclobutane or olefin products under the pyrolysis conditions.

(19) The azo generated diradical is either not formed "hot" or if "hot" the excess vibrational energy has no substantial chemical consequences.

(20) Hydroboration of 3-methyl-*cis-* and *-trans*-1,3-pentadiene followed by oxidation afforded *erythro-* and *threo*-3-methylpentane-1,4-diol. Reaction of the corresponding erythro and threo diol dimethanesulfonates with dimethylhydrazo-1,2-dicarboxylate and sodium hydride afforded dimethyl *trans-* and *-cis*-3,4-dimethyltetrahydropyridazine-1,2-dicarboxylates.[14] The cis and trans diurethanes were further separated by preparative vapor phase chromatography (≥99.5% isomeric purities). These diurethanes gave satisfactory C,H analysis and spectral data.

(21) These azo compounds suffered facile irreversible azo to hydrazone tautomerization in the presence of trace amounts of acid, base, solvents, and light.

(22) Product ratios were insensitive to changes in surface area and pressure (30–500 mm). Decomposition in benzene (sealed tubes) at 306° gave similar results. Control experiments show that the hydrocarbon products are stable under the pyrolysis conditions. Hydrazone by-product was shown not to give cyclobutane or olefin products under the pyrolysis conditions.

(23) From azo-6 *trans/cis*-2-butene 68.6/5.2 (observed) = 36.6 (direct) + 32.0/5.2 (diradical) and from azo-**5** *cis/trans*-2-butene 64.0/11.3 (observed) = 35.4 (direct) + 28.6/11.3 (diradical).

(24) The hot diradical postulate proposes the vibrationally hot 1,4-diradicals have $k(\text{rotation}) \ll k(\text{closure}) \sim k(\text{cleavage})$ from $A(\text{rotation}) \ll A(\text{closure}) \sim A(\text{cleavage})$.[8,3a] An attempt to fit the azo data to the hot diradical postulate would require $A(\text{rotation}) \sim A(\text{closure}) \ll A(\text{cleavage})$.

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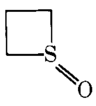
Received September 18, 1975

Sulfine[1]

Sir:

While a wide variety of substituted sulfines are known and are generally described as stable substances,[2] the parent compound, CH_2SO, has thus far eluded synthesis.[2a,3] We now wish to report the facile generation of sulfine (thioformaldehyde *S*-oxide) by flash vacuum pyrolysis (FVP) of a number of readily available precursors. We also report herein the structure of this intriguing molecule as determined by microwave spectroscopy.

In view of the demonstrated generation of other elusive "heteroolefinic" species by pyrolysis or photolysis of various four-membered rings,[4] heterocyclobutanes **1** and **2** seemed to be likely sulfine precursors. Indeed, initial study of the FVP of thietane *S*-oxide (**1**)[5] and 1,3-dithietane 1-oxide (**2**)[6] (utilizing a pyrolysis system[7] connected directly to the source of a mass spectrometer) suggested that both compounds decomposed cleanly to sulfine in the gas phase beginning at temperatures of ca. 600° and 300°, respectively. Definitive evidence for the formation of sulfine from **1** and **2** under FVP conditions was obtained by following the decomposition of **1** and **2** by microwave spectroscopy. Thus, when **2** at its vapor pressure of 25μ was evaporated through a pyrolysis tube into a microwave absorption cell, generation of sulfine was detected first at a pyrolysis temperature of 300 °C and was complete above 500° at which temperature the spectrum of **2**[6] had been replaced by the spectra of thioformaldehyde[8] and sulfine.



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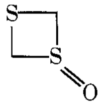

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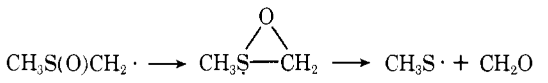
A number of other possible precursors of sulfine were examined using FVP-mass spectrometry and FVP-microwave spectroscopy techniques. Pyrolysis of 1,3,5-trithiane has been shown to generate thioformaldehyde.[8] We find that sulfine is produced, albeit inefficiently, on FVP of 1,3,5-trithiane 1-oxide.[9] The pyrolysis of Me_2SO is suggested to involve a chain decomposition with sulfine as one intermediate (eq 1–3).[10]

$$CH_3S(O)CH_3 \xrightarrow{\Delta} CH_3SO\cdot + CH_3\cdot \qquad (1)$$

$$CH_3S(O)CH_3 + CH_3\cdot \longrightarrow CH_4 + CH_3S(O)CH_2\cdot \qquad (2)$$

$$\underset{\mathbf{3}}{CH_3S(O)CH_2\cdot} \longrightarrow CH_3\cdot + CH_2SO \qquad (3)$$

In our hands FVP of Me_2SO at 650° did in fact generate sulfine, though not as efficiently as did FVP of **2**. Since Gollnick[11] has postulated that radical **3**, when generated by photolysis of neat Me_2SO, undergoes an alternative mode of decomposition than that indicated by eq 3, namely, rearrangement followed by fragmentation (eq 4), it seemed desirable to provide additional support for the thermal radical fragmentation process of eq 3. Iodomethylmethyl sulfoxide (**4**)[12] appeared to be a suitable precursor to radical **3.** FVP of **4** at 350° did indeed generate sulfine together with methyl iodide (both rather inefficiently), perhaps via the sequence of reactions indicated in eq 5–7.



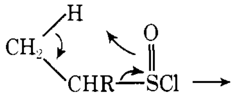
$$CH_3S(O)CH_2\cdot \longrightarrow CH_3\overset{O}{S{-}CH_2} \longrightarrow CH_3S\cdot + CH_2O \qquad (4)$$

$$CH_3S(O)CH_2I\ (\mathbf{4}) \xrightarrow{\Delta} CH_3S(O)CH_2\cdot + I\cdot \qquad (5)$$

$$CH_3S(O)CH_2\cdot \longrightarrow CH_2SO + CH_3\cdot \qquad (6)$$

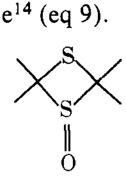
$$CH_3S(O)CH_2I + CH_3\cdot \longrightarrow CH_3S(O)CH_2\cdot + CH_3I \qquad (7)$$

Base induced dehydrochlorination of alkane- or arylalkanesulfinyl chlorides has been widely used to generate substituted sulfines,[2a,c,d,g] although the reaction reportedly fails with methanesulfinyl chloride.[2a,3] We find that FVP of methanesulfinyl chloride at 600° affords HCl and sulfine. In examining FVP routes to sulfine homologues, we find that FVP of ethanesulfinyl chloride and 2-propanesulfinyl chloride affords HCl, ethylene or propene (respectively) and SO_2 and S_2O (presumably derived from decomposition of SO[13]), perhaps via a Cope-elimination (eq 8).



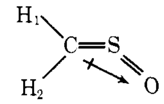
$$\longrightarrow RCH{=}CH_2 + [HOSCl] \longrightarrow HCl + SO \quad (8)$$

We have, however, succeeded in generating a sulfine homologue, thioacetone *S*-oxide,[2] by a cycloreversion route, namely, FVP of 2,2,4,4-tetramethyl-1,3-dithietane 1-oxide[14] (eq 9).



$$\xrightarrow[400°]{\text{FVP}} (CH_3)_2C{=}S + (CH_3)_2C{=}S{=}O \quad (9)$$

Microwave study of the pyrolysis products of 1,3-dithietane-d_2 1-oxide, -d_4 1-oxide, and -d_4 1-oxide-^{18}O,[6] Me_2SO-d_6 and -^{18}O[16] as well as the normal species led to the assignment of seven isotopic modifications of sulfine (d_1-syn, d_1-anti, d_2,^{18}O, ^{34}S, ^{13}C, and d_2 ^{34}S; ^{34}S and ^{13}C determined in natural abundance). These and the normal species assignment result in the following "substitution structure" for sulfine (labeled as in **5**):[17] C–H_2 = 1.085 (0.002) Å, C–H_1 = 1.077 (0.002) Å, C–S = 1.610 (0.004) Å, S–O = 1.469 (0.004) Å, $\angle H_1CH_2$ = 121.86 (0.04)°, $\angle H_2CS$ = 122.51 (0.08)°, $\angle H_1CS$ = 115.63 (0.10)°, and $\angle CSO$ = 114.72 (0.04)° (the uncertainty, estimated as twice the standard deviation, is given in parentheses).[18] By way of comparison the geometry of thioformaldehyde is C–H = 1.093 Å, C–S = 1.611 Å, and $\angle HCH$ = 116.87°.[8] Sulfine is planar with a dipole moment of 2.994 D oriented 25.50° relative to the S–O bond as shown in **5** (the indicated polarity is assumed).[20] The gas-phase infrared spectrum of sulfine exhibits two strong vibration-rotation bands with prominent Q-branches centered at 1170 and 760 cm^{-1}. The former frequency is characteristic of the C=S=O group.[2g,21]



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The decomposition of sulfine in the gas phase could be conveniently studied by following the disappearance of the sulfine absorption lines in a closed microwave cell. In a cell free of polymeric decomposition products, sulfine at a pressure of 30 μ decayed linearly with a 30-min lifetime. After the cell had been used for several weeks, sulfine's decomposition was exponential in the 30–300 μ pressure range, with a half-life of ca. 1 h (under the latter conditions, the lifetime of thioformaldehyde was found to be ca. 20 s[22]). The principal gaseous decomposition products were CH_2O and SO_2. The reactions and mechanism of decomposition of sulfine are currently under investigation.

It might be noted that since sulfine is the *S*-oxide of thioformaldehyde, which has been established as a constituent of the interstellar medium,[23] sulfine itself might be of some astronomical significance.

Acknowledgment. Support for this research by the Research Corporation (R.E.P) and the National Science Foundation under its Undergraduate Research Participation program is gratefully acknowledged. We thank Mr. W. Garrison and Mr. T. Renken for technical assistance.

References and Notes

(1) Paper 1 of the series "The Chemistry of Sulfines".
(2) For example, see (a) W. A. Sheppard and J. Diekmann, *J. Am. Chem. Soc.*, **86**, 1891 (1964); (b) W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *J. Org. Chem.*, **30**, 3071 (1965); (c) G. Opitz, *Angew Chem., Int. Ed. Engl.*, **6**, 107 (1967); (d) B. Zwanenburg and J. Strating, *Q. Rep. Sulfur Chem.*, **5**, 79 (1970); (e) C. N. Skold and R. H. Schlessinger, *Tetrahedron Lett.*, 791 (1970); (f) H. H. Wasserman and W. Strehlow, *ibid.*, 795 (1970); (g) M. H. Brodnitz and J. V. Pascale, *J. Agr. Food Chem.*, **19**, 269 (1971); (h) B. Zwanenburg, L. Thijs, J. B. Broens, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **91**, 443 (1972); (i) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, 539 (1975); (j) D. H. R. Barton, L. S. L. Choi, R. H. Hesse, M. M. Pechet, and C. Wilshire, *ibid.*, 557 (1975).
(3) (a) W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3231 (1963); (b) S. Schuring, Diploma Thesis, Universität Tubingen, 1963 (cited in reference 2c).
(4) For examples, see (a) A. Jones and F. P. Lossing, *J. Phys. Chem.*, **71**, 4111 (1967); (b) R. Langendries, F. C. De Schryver, P. de Mayo, R. A. Marty, and J. Schutyser, *J. Am. Chem. Soc.*, **96**, 2964 (1974); (c) L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8**, 18 (1975); (d) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **97**, 7371 (1975).
(5) A. Cerniani, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90**, 382 (1960).
(6) The previously unknown 1,3-dithietane 1-oxide **2** has been synthesized through reaction of bis(chloromethyl) sulfoxide with sodium sulfide. Details of the preparation, reactions, and structure of **2** and its various derivatives will be the subject of forthcoming publications.
(7) The apparatus consisted of a solid probe for an A.E.I. MS-12 mass spectrometer hollowed to accept a length of electrically heated heavy wall 2-mm quartz capillary fitted with a chromel alumel thermocouple. The samples were evaporated at low pressure through the capillary and mass spectra were recorded at low ionizing voltage as a function of temperature. With the compounds studied the growth in intensity of the *m/e* 62 peak (CH_2SO) was coupled with the disappearance of the original parent ion and its fragment peaks.
(8) D. R. Johnson, F. X. Powell, and W. H. Kirchhoff, *J. Mol. Spectrosc.*, **39**, 136 (1971).
(9) E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 15 (1929).
(10) F. C. Thyrion and G. Debecker, *Int. J. Chem. Kinet.*, **5**, 583 (1973).
(11) K. Gollnick and H. U. Stracke, *Pure Appl. Chem.*, **33**, 217 (1973).
(12) C. G. Venier and H. J. Barager, III, *J. Chem. Soc., Chem. Commun.*, 319 (1973).
(13) P. W. Schenk and R. Steudel, *Angew. Chem., Int. Ed. Engl.*, **4**, 402 (1965).
(14) Prepared by peracetic acid oxidation of 2,2,4,4-tetramethyl-1,3-dithietane.[15]
(15) T. Nishio, M. Yoshioka, H. Aoyama, and N. Sugiyama, *Bull. Chem. Soc. Jpn.*, **46**, 2253 (1973).
(16) N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).
(17) Full details of the microwave structural study of sulfine will appear elsewhere: R. E. Penn and R. J. Olsen, *J. Mol. Spectrosc.*, in press.
(18) The structure of sulfine is very similar to the C=S=O portion of the compound *cis*-mesityl(phenylsulfonyl)sulfine, recently determined by x-ray crystallography.[19]
(19) Th. W. Hummelink, *J. Cryst. Mol. Struct.*, **4**, 87 (1974).
(20) The indicated dipole moment can be resolved into a component along the C–S bond of the same magnitude as thioformaldehyde (ca. 1.6 D[8]) plus a 2 D vector oriented along the S–O bond.
(21) An analysis of the photoelectron spectrum of sulfine will be presented elsewhere: H. Bock, P. Rosmus, B. Solouki, and E. Block, manuscript in preparation.
(22) The half-life of thioformaldehyde under somewhat similar conditions has been reported to be 6 min.[8]
(23) M. W. Sinclair, J. C. Ribes, N. Fourikis, R. D. Brown, and P. D. Godfrey, *Int. Astron. Union, Circ.*, No. 2362, Nov 1971.
(24) National Science Foundation Undergraduate Research Participant, 1975.

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Received October 15, 1975

Trimethylsilylpotassium. Deoxygenation of Epoxides with Inversion of Stereochemistry

Sir:

The reactions of silyl anions with appropriately substituted epoxides are potential stereospecific routes to diastereomerically pure erythro and threo-β-alkoxysilanes.[1] We report here that some mono-, di-, and trisubstituted ep-